

Catalyst Deactivation due to Pore-plugging by Reaction Products

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INTRODUCTION

The regulation of sulfur oxide emissions from the combustion of fuels is directed primarily at high sulfur content coal and residual fuel oil [1]. Of the four basic sources of primary energy, heavy fuel oil may be the best hope for meeting sharply increasing energy demands in the near future [2]. The above two factors combined, lead to significant interest in methods of heavy fuel oil desulfurisation. One method for removing sulfur from fuel oil is trickle-bed hydrodesulfurisation. Hydrogen and oil are passed cocurrent downflow over a fixed bed of catalyst at elevated temperatures and pressures. This approach has recently been commercially proven [3]. Hydrotreating of residuum oils in this way has revealed the presence of (undesirable) demetallation reactions taking place in parallel with the desired desulfurisation reactions [4]. Organometallic constituents of the oil, primarily vanadium, nickel and iron, react out of the oil and combine with hydrogen sulfide to produce solid deposits of metal sulfides. The deposition of these reaction products occur both inter and intra-particle. The intra-particle deposits decrease the effective diffusivity of the catalyst particles for desulfurisation, thus causing deactivation by a pore-plugging mechanism [5]. In this earlier paper approximate methods were outlined to predict catalyst life for various feed-stocks at a particular liquid hourly space velocity (LHSV) and desulfurisation conversion. However, predictions were based on pore diffusion theory, initially developed by Thiele [6], so that no particular pore model was required. This meant that catalysts with different pore size distribution could not be ranked for desulfurisation performance. In addition, pore plugging effects were averaged over the entire reactor length. A better approach would be to look more closely at the top of the reactor where the metals deposition rate is greatest. If pore plugging by metals is considered to be the primary mode of catalyst deactivation, the deactivation wave would probably begin at the top of the bed and then sweep down the reactor.

This paper considers catalyst deactivation in residuum hydrodesulfurisation by a pore-plugging mechanism in combination with coking effects. Simple catalyst pore size distributions are compared in desulfurisation service. Process conditions are varied to show their influence on catalyst lives. Predictions are compared with some available commercial data.

PROPOSED MODEL FOR CATALYST DEACTIVATION

The pore-plugging concept was proposed some years ago by Hiemenz [7] on the basis of gas permeability measurements on fresh and used catalyst pellets. Beuther and Schmid [8] compared the effects of coke deposits on the physical properties of various HDS catalysts. By comparing the surface areas and pore size distributions of fresh and spent catalysts, it was shown that the average pore radius was reduced only slightly

and that the pore size distribution maintained approximately the same percentage distribution in spite of a considerable reduction in surface area. It was observed that the coke content of the catalyst increased sharply to an equilibrium level in a short time, about 40 hours. It was postulated that this was due to a period of uncontrolled hydrocracking. Subsequently, the coke content of the catalyst was observed to remain constant with increasing process time.

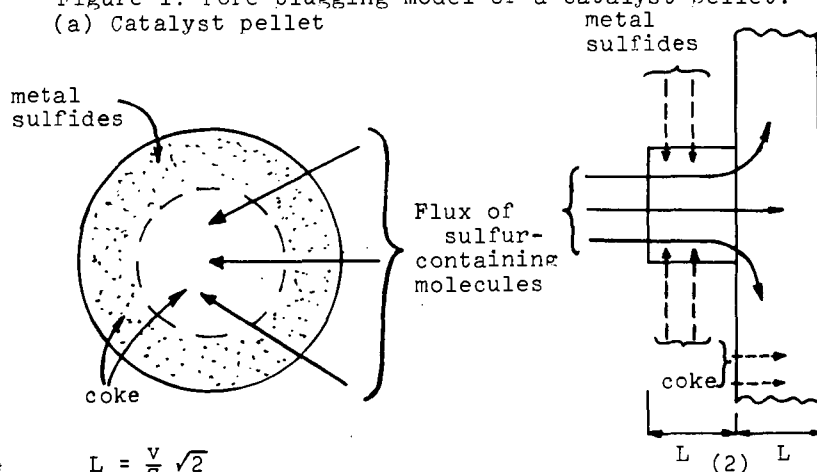
It is therefore proposed that the porosity of the catalyst is made up of three parts.

$$\theta = \theta_{c_I} + \theta_{c_E} + \theta_{MS} \quad (1)$$

Rapid, initial coke deposition (θ_{c_I}) takes up about one-third of the total porosity. Equilibrium coke deposition (θ_{c_E}) and metal sulfides plugging (θ_{MS}) then slowly decrease the remainder of the catalyst porosity. This slow utilisation of porosity is incorporated into a pore-plugging model. The latter assumes that only a fraction of the pellet is effective for the demetallation reactions. The flux of sulfur-containing molecules into the pellet is progressively impeded by the deposition of metal sulfides and coke in the catalyst pores. Figure 1(a).

The basis for the pore structure is Wheeler's model [9]. The pellet is approximated as a composite of N pores each of length L . Figure 1(b).

Figure 1: Pore-plugging model of a catalyst pellet.
(a) Catalyst pellet



where

$$L = \frac{V}{S} \sqrt{2}$$

$$N = \frac{S \theta(r)}{\pi r^2 \sqrt{2}} = \frac{K_1}{r^2} \quad (3)$$

The pore wall is not a continuous solid but has many intersections with other pores. The constant K_1 is a catalyst parameter and reflects the size and shape of the pellet together with its pore size distribution. The nature of the pore-plugging model suggests that the number of pores effective for demetallation (N_E) is some fraction of the total given by

$$N_E = \eta N \quad (4)$$

η refers to a time averaged effectiveness factor based typically on electron micro-probe analyses of metals profiles in spent catalyst from one long life test. Other catalysts with different pore size distributions can be compared with the experimental catalyst for potential demetallation capacity by

$$N_{E,B} = \frac{|\Theta(r)|_B}{|\Theta(r)|_A} \cdot N_{E,A} \quad (5)$$

Pore size distributions used in this paper are kept simple and follow Wheeler's approach [9]. For a Maxwellian distribution of pore sizes

$$L_M(r) = A_M \frac{r}{r_0} e^{-r/r_0} \quad (6)$$

r_0 is the most probable pore radius and is related to average catalyst properties by

$$\bar{r} = 3r_0 = 2 \frac{V_g}{S_g} \quad (7)$$

The corresponding pore volume distribution is

$$\Theta_M(r) = \int \pi r^2 \cdot L_M(r) \cdot dr \quad (8)$$

The Maxwellian or log normal distributions are considered since the pore size distribution of some hydrodesulfurisation catalysts can be approximated in this way [10]. For a Gaussian distribution of pore sizes

$$L_G(r) = A_G \exp -\beta^2 \left(\frac{r}{r_0} - 1 \right)^2 \quad (9)$$

$$\bar{r} = r_0 \left| 1 + \frac{1}{2\beta^2} \right| = 2 \frac{V_g}{S_g} \quad (10)$$

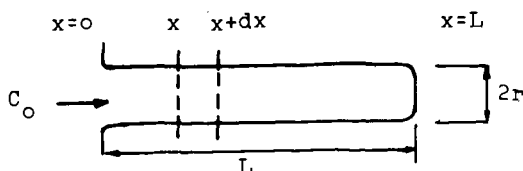
$$\Theta_G(r) = \int \pi r^2 \cdot L_G(r) \cdot dr \quad (11)$$

β is a parameter of sharpness for the distribution. Wheeler showed that many gel type catalysts have this type of pore size distribution [9].

THE DEACTIVATION RATE

Reaction parameters are now considered using an elementary solution for diffusion and reaction in pores which are less than about 50% available to the reaction [9]. This can be justified from preliminary estimates for catalyst life [5].

Figure 2: Diffusion and reaction in a cylindrical pore.



Considering a first order, irreversible reaction in a cylindrical pore and balancing the net influx against the rate of reaction

$$\pi r^2 D \left| \left(\frac{dc}{dx} \right)_x - \left(\frac{dc}{dx} \right)_{x+dx} \right| = 2\pi r dx k c(x) \quad (12)$$

Dividing through by dx and letting $dx \rightarrow 0$,

$$\pi r^2 D \frac{d^2 c}{dx^2} = 2\pi r k c(x) \quad (13)$$

This is the fundamental differential equation that is usually solved. However, when all the reactant diffusing into the pore is consumed at some distance $x_p \ll L$, then equation (12) can be simplified to

$$\pi r^2 D \left(\frac{dc}{dx} \right)_{x=0} = 2\pi r k \int_0^{x_p} C(x) dx \quad (14)$$

Now $\left(\frac{dc}{dx} \right)_{x=0}$ can be approximated by $\frac{C_0}{x_p}$ and the exact reaction rate

on the pore wall can be approximated by $2\pi r k \frac{C_0}{2}$. Equation (13) is reduced to $\pi r^2 D \frac{C_0}{x_p} = 2\pi r x_p k \frac{C_0}{2}$ (15)

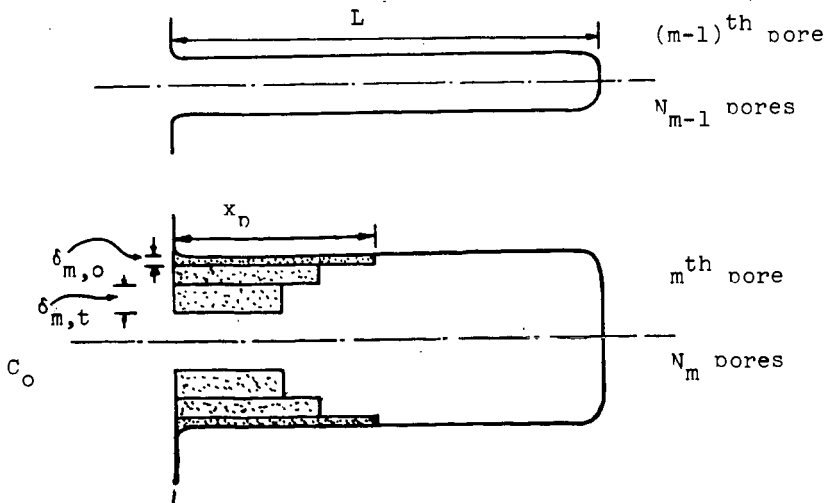
where x_p is the penetration length.

$$x_p = \sqrt{\frac{D}{k}} r = K_2 \sqrt{r} \quad (16)$$

The constant K_2 is dependent on feed type and process conditions both of which determine the demetallation reaction rate.

If the decay of catalyst is slow relative to the oil residence time, a quasi steady state assumption can be made to determine the decrease in pore radii due to deposition of reaction products i.e. coke and metal sulfides. This will then be related to catalyst deactivation.

Figure 3: Deposition of reaction products in catalyst pores.



If the plugging material is spread over all the pores contained in the outer section of the pellet, then the thickness of deposit δ_t for a finite increment of time Δ is given by

$$\delta_t = \frac{(Pl)_{\Delta}}{2\pi \sum_m N_{E,m} r_{m,t} x_{m,t}} \quad (17)$$

and

$$N_{E,m} = \frac{S(\theta - \theta_c) \eta}{\pi r_m^2 \sqrt{2}} \quad (18)$$

$$r_{m,t} = r_{m,0} - \sum_0^{t-\Delta} \delta_t \quad (19)$$

$$x_{m,t} = K_2 \sqrt{r_{m,t-\Delta}} \quad (20)$$

Assuming that the demetallation and desulfurisation functions of the catalyst are deactivating at approximately the same rate [11], then demetallation can be used to follow desulfurisation fouling rates. Since the overall demetallation rate equals the flux of metal containing molecules into the pellet,

$$[R_{HDM}]_t = F_t = \sum_m \frac{N_{E,m} r_{m,t}^2}{x_{m,t}} \quad (21)$$

F_t/F_0 is a measure of the decrease in reaction rate due to pore plugging. In constant conversion operation this is usually compensated by raising catalyst temperature. Assuming a power law deactivation function

$$Y \propto R_{HDM}^2 \propto R_{HDS}^2 \quad (22)$$

then

$$Z = \left[\frac{F_0}{F_t} \right]^2 \quad (23)$$

represents the number of times the initial deactivation rate is increased. F_0 is known from the fresh catalyst properties and specified process conditions. F_t can be calculated at any time onstream so that a curve of deactivation rate ratio versus process time can be constructed. A value of 5-10 for this ratio will probably mean end-of-run under practical conditions.

THE PORE PLUGGING RATE

The rate of deposition of reaction products i.e. coke plus metal sulfides, can be estimated from the kinetics of the respective processes. Demetallation like desulfurisation can be represented by second order kinetics [8], the apparent anomaly being explained by considering the oil as a spectrum of compounds reacting at different rates. The equality of desulfurisation and demetallation selectivities is also well known for a wide range of crude oil sources [12].

For an ideal, plug flow reactor operating at steady state, isothermal operation may be assumed for finite volume element of reactor of length Δl . Considering an irreversible, second order, demetallation reaction taking place in the catalyst pores, a mass balance for reactant i gives

$$\text{In: } (\text{LHSV}) \frac{\rho_F}{\rho_B} \frac{C_{Fi}}{1 + C_{Fi} k_2 \tau \left(\frac{1}{L} \right)} \quad (24)$$

$$\text{Out: } (\text{LHSV}) \frac{\rho_F}{\rho_B} \frac{C_{Fi}}{1 + C_{Fi} k_2 \tau \left(\frac{1 + \Delta L}{L} \right)} \quad (25)$$

At the top of the reactor where $\frac{1}{L} = 0$, the rate of deposition of metal sulfides in the first layer is

$$R_{MS_i} = M_i (\text{LHSV}) \frac{\rho_F}{\rho_B} C_{Fi} \frac{C_{Fi} k_2 \tau \left(\frac{\Delta L}{L} \right)}{1 + C_{Fi} k_2 \tau \left(\frac{\Delta L}{L} \right)} \quad (26)$$

The contribution to the pore-plugging rate from the metal sulfides is the sum of all the depositing sulfides divided by a density factor

$$Pl_{MS} = \frac{d}{\rho_{MS}} \sum_{i=1}^n R_{MS_i} \quad (27)$$

n is usually equal to 2 i.e. vanadium and nickel. ρ_{MS} was assigned a value of 2 gm/cc based on earlier estimates [5]. A distribution factor d is included to distinguish between metals depositing intra-particle and interparticle. Based on vanadium and nickel concentrations in the asphaltenes and maltenes fraction of oils, this factor is assumed to be 0.8 for a Safaniya atmospheric residuum.

The coke contribution to the pore-plugging rate can be deduced from the observed constancy in coke content of the desulfurisation catalyst during 40-400 hours of operation [8] and 50-1000 hours of operation [13]. At any time on-stream greater than 50 hours, it follows that

$$Q\% \text{ coke} = \frac{W_c}{W_f + W_c + W_{MS}} = \text{constant} \quad (28)$$

Since the metal sulfides deposition rate is constant in constant conversion operation, the coking rate can be calculated from equation (28) with some modifications

$$\frac{W_{c1} + \int_{50}^t R_c dt}{W_f + W_{c1} + \int_{50}^t R_c dt + R_{MS} \cdot t} = Q \quad (29)$$

W_c represents the rapid initial coke lay-down already described [8]. For small t (< 50 hours), $R_{MS} t \rightarrow 0$, so that W_f may be found if Q is specified. A typical value for Q would be 10 weight per cent coke. For $t > 50$ hours, R_c can be written in terms of R_{MS}

$$R_c = \left(\frac{Q}{1-Q} \right) R_{MS} \quad (30)$$

The pore plugging rate due to coke can now be calculated using a coke density (ρ_c) derived from two sets of data [8]. A value of 0.7 gm/cc was calculated.

$$(Pl)_c = \frac{1}{\rho_c} \left(\frac{Q}{1-Q} \right) R_{MS} \quad (31)$$

The total pore-plugging rate is given by

$$(Pl)_T = (Pl)_c + (Pl)_{MS} \quad (32)$$

For 10 weight per cent coke on the catalyst, a total pore plugging rate of $\approx 1.3 R_{MS}$ is calculated.

The total pore-plugging rate is put into equation (17) to determine the reduction in pore radii over the whole pore size distribution, equation (6) for example. The decrease in radius will reduce the flux of metal containing molecules into the pores, equation (21). This flux is compared with the initial value to calculate the catalyst deactivation with time from equation (23).

MAIN ASSUMPTIONS FOR RDS APPLICATIONS

To facilitate catalyst comparisons only one particular oil feedstock is considered, Safaniya (Khafji) atmospheric residuum. Its sulfur content is usually 4 weight per cent with vanadium and nickel contents of about 75 and 25 ppm respectively. Deposited sulfides were assumed to have the formulae V_2S_3 and NiS .

The desulfurisation performance for various catalysts was compared by coupling their demetallation and desulfurisation functions. For a Safaniya atmospheric residuum at LHSV=1.0 and a desulfurisation conversion of 75%, effective diffusivity values of 6×10^{-8} and 3×10^{-7} cm^2/sec . were estimated for demetallation and desulfurisation respectively [5]. Figure 4 was constructed from the equation [6].

$$\Phi = \frac{R^2}{D_{eff}} \left(R_{HDM} \right) \frac{1}{C_0} \quad (33)$$

where

$$D_{eff} = \frac{D(\theta - \theta_{CI})}{2} \quad (34)$$

From Figure 4, effectiveness factors for demetallation and desulfurisation were found to be 0.1 and 0.45 for a 0.16 cm (1/16 inch) diameter sphere. Subsequent process condition changes leading to temperature changes were made by modifying the intrinsic activation energy using the equation [14].

$$\frac{E_{INT}}{E_{OBS}} = 2 - \eta \quad (35)$$

Intrinsic activation energies for demetallation and desulfurisation were chosen as 30 and 40 kcal/gram mole. The latter value is realistic based on recent literature [15] when a value of 38 kcal/gram mole was measured. The former value reflects the fact that metal-containing molecules are derived from the heavier portion of the feedstock (550°C+) whereas the sulfur-containing molecules are derived from the whole boiling range (325°C+) of the oil.

At process conditions of LHSV=1.0, 75% conversion and 1500 psig, the coke level on the catalyst was assumed to be 10% by weight [13]. This level was adjusted for temperature changes using the temperature dependence of coke content found by Voorhies [16].

A "standard" catalyst whose properties could be considered suitable for hydrodesulfurisation was selected for the purpose of making catalyst life predictions. Its properties are shown in Table 1 together with properties of two other catalyst which were also considered.

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Table 1

Catalyst	"Standard"	Macropores	\bar{r} - shift
r (Angstroms)	40	40	65
V_g (micropores)	0.5	0.425	0.7
S_g m^2/gm	250	212	215
R cm	0.08	0.08	0.08
f_B	0.7	0.59	0.57
f_P	1.2	1.02	0.97
shape	sphere	sphere	sphere
β	5	5	5
% macropores (> 600 A)	0	15	0

The above catalyst properties were inter-related by the equation

$$\frac{1}{f_P} - \frac{1}{f_S} = V_g \quad (36)$$

Pore Volume distributions of the catalysts considered subsequently are shown in Figure 5.

DISCUSSION OF MODEL PREDICTIONS

The effect of changing process conditions on catalyst life is shown in Figure 6. The deactivation rate ratio is plotted versus hours on-stream. At an LHSV = 1.0 and 75% conversion, a catalyst life of 1000 hours is predicted. This compares with about 3300 hours ($z=5$) when the conversion is dropped to 63%. Another curve, LHSV = 0.7 and 75% conversion is shown in Figure 6. These conditions were chosen for comparison with data from the Gulf Tokyo paper [4], Figure 4 and Table 6. From these data the conversion of 75% was given but only a "fixed" space velocity is mentioned. This has been assumed to be 0.7. With this assumption, the pore-plugging model suggests a life of 4000 hours compared to 4500-5000 hours from the Gulf Tokyo paper. Obviously more information on catalyst properties and process conditions is required when commercial data is published. However, the pore-plugging model and the initial assumptions give good order-of-magnitude comparisons.

The effects of changing the pore size distribution of the "standard" catalyst and \bar{r} -shift are shown in Figure 7. For a fixed average pore diameter, changing pore size distribution has little effect on catalyst life. The log normal or Maxwellian distribution may have been predicted to give an increased life because of the "tail" in the distribution but since the most probable pore radius is only $15A (=r_0)$, the advantage of the broader distribution is lost. If the peak radii, normal versus log normal were both the same, then the broader distribution could be more effective. With a normal distribution, increasing the average pore radius has a big effect on catalyst life. A value of 2000 hours is predicted for the \bar{r} -shift catalyst in Table 1. This order of magnitude effect has been observed for this feedstock at these conditions [17] but complete data is not available.

Putting macropores into the catalyst or decreasing pellet diameter also increases catalyst life. The net effect in both cases is to substantially increase the number of pores available for metal sulfides deposition. In Table 1, 15% macropores have been substituted for micropore volume and it is assumed that an increase in effective diffusivity of ($\times 3$) is obtained. In Figure 8, a catalyst life of 2000 hours is predicted compared to 1000 hours for the zero-macropores "standard" catalyst. Particle size effects are greater since the increase in number of available pores is effective on the unchanged "standard" catalyst micro-

porosity (≈ 0.6). A life of 3000 hours is predicted i.e. an increase of ($\times 3$) when pellet diameter is reduced by ($\times 2$). If reactor pressure drop problems are likely, then macropores must be considered first for increasing catalyst life. The approach is limited however by the decreasing strength of the pellet as porosity is increased. Alternatively, changing reactor design, radial flow instead of axial flow [18], would allow smaller particles to be used, about 0.5 mm diameter. Catalyst life would then be substantially increased.

Catalyst changes have previously been physical in nature i.e. macropores, r -shift and particle size. The chemical composition of the catalyst was not changed. The role of coke in pore-plugging does suggest that increasing the hydrogenation function of the catalyst may increase catalyst life e.g. nickel as a "kicker". If nickel was substituted for part of the cobalt then some desulfurisation activity might be lost since the optimum cobalt/molybdenum ratio has been changed [19]. The net effect would be to lose some initial activity but more micro-porosity would be available due to a lower equilibrium coke level on the catalyst. This is the basis for Figure 9 when the coke level of the "standard" catalyst was assumed to be reduced from 10% to 7% due to increasing the hydrogenation function of the catalyst. The catalyst life is seen to be increased from 1000 to 1500 hours ($z=5$).

The effect of changing process pressure also illustrates the coke contribution to the pore plugging deactivation model. Figure 9 shows that reducing pressure from 1500 psig to 800 psig decreases catalyst life by ($\times 2$). An obvious way to compensate is by decreasing LHSV e.g. from 0.7 to 0.5, a ratio of 1.4. At the lower space velocity, a prediction of 5000 hours is obtained and the catalyst life is now close to the 1500 psig case. This space velocity effect with pressure compares favorably with the Esso Tokyo paper, Figure 7, [4]. Data showed that catalyst life was the same when operating at 1500 and 800 psig provided space velocity compensation was employed. The relative catalyst activity in the Esso data was also about 1.4.

CONCLUSIONS

A pore-plugging model for residuum hydroprocessing in axial-flow trickle-bed reactors has been proposed in order to quantitatively describe catalyst deactivation. The pore-plugging is due to the deposition of reaction products, metal sulfides and coke, during the (desired) desulfurisation reaction. The desulfurisation and demetallation reactions were considered in parallel in order to make predictions for catalyst life. A simplified approach was taken in describing catalyst pore size distributions and approximating the equations for diffusion and reaction in a catalyst pore.

Predictions for catalyst life were made when process conditions and catalyst parameters were changed. As a check on the initial assumptions and the simplified approach, comparison with commercial data was made and showed good order-of-magnitude agreement.

A more rigorous approach should now be considered as more data becomes available. Design of new and improved catalysts and reactor systems should be the result.

NOMENCLATURE

A_M, A_G	absolute frequency of pore sizes
C	concentration of reactant, metal containing molecules, inside the catalyst pores, mol. cm^{-3} .
C_0	concentration of reactant at the pore mouth, mol. cm^{-3} .
D	diffusivity of metal containing molecules in the oil, $\text{cm}^2 \text{sec}^{-1}$.
F_t	flux of metal containing molecules into the pellet at time t , mols. $\text{hr}^{-1} \text{gm}^{-1}$.
k	first order intrinsic reaction rate constant, cm sec^{-1} .
k_2	second order reaction rate constant, $\text{cm}^3 \text{hr}^{-1} \text{mol}^{-1}$.
K_1	catalyst parameter, equation (3), $\text{cm}^2 \text{gm}^{-1}$.
K_2	pore penetration parameter, equation (16), cm.
L	pore length, equation (2), cm.
$L_M(r)$	total length of pores of radius r per gram of catalyst in Maxwellian distribution, cm gm^{-1} .
n	number of reactants in the feed.
N	total number of pores per gram of catalyst, equation (3), gm^{-1} .
N_E	number of pores per gram of catalyst in which pore plugging occurs, equation (4), gm^{-1} .
Pl_{MS}	metal sulfide pore plugging rate, $\text{cm}^3 \text{hr}^{-1} \text{gm}^{-1}$.
Pl_c	coke pore plugging rate, $\text{cm}^3 \text{hr}^{-1} \text{gm}^{-1}$.
Pl_T	total pore plugging rate.
Q	coke on catalyst, % by weight.
r	pore radius, cm.
r_0	most probable pore radius in Maxwellian pore size distribution, cm.
R_{HDS}	desulfurisation rate, mol. $\text{hr}^{-1} \text{gm}^{-1}$.
R_{HDM}	demetallation rate, mol. $\text{hr}^{-1} \text{gm}^{-1}$.
R_{MS}	metal sulfides deposition rate hr^{-1} .
R_c	coke deposition rate, hr^{-1} .
S	pellet surface area, cm^2 .
S_g	catalyst surface area, $\text{cm}^2 \text{gm}^{-1}$.
v	pellet volume, cm^3 .
V_g	catalyst pore volume, $\text{cm}^3 \text{gm}^{-1}$.
w_f	fresh catalyst weight, gm.
w_c	coke weight, gm.
w_{MS}	metal sulfides weight, gm.
$(LHSV)$	reactant penetration length into the pore, liquid hourly space velocity, hr^{-1} .
D_{eff}	effective diffusivity of catalyst pellet, equation (34), $\text{cm}^2 \text{sec}^{-1}$.
E_{INT}	intrinsic activation energy kcal. gm mol^{-1} .
E_{OBS}	observed activation energy kcal. gm mol^{-1} .
R	radius of catalyst pellet, cm.
Z	catalyst deactivation rate ratio.

NOMENCLATURE

Greek letters.

δ	thickness of deposit in catalyst pores, cm.
Δ	element of time for reaction, hr.
Δl	length of volume element in plug flow reactor, cm.
θ	total catalyst porosity.
θ_{cI}	catalyst porosity lost to coke during rapid initial deactivation.
θ_{cE}	catalyst porosity lost to coke after initial coke formation.
θ_{MS}	catalyst porosity lost to metal sulfides after initial coke formation.
η	"time averaged" effectiveness factor.
ρ_c	coke density, gm. cc ⁻¹ .
ρ_B	catalyst bulk density, gm, cc ⁻¹ .
ρ_F	density of feed stream, gm cc ⁻¹ .
ρ_{MS}	metal sulfides density, gm. cc ⁻¹ .
ρ_P	catalyst particle density gm cc ⁻¹ .
ρ_S	catalyst skeletal density gm cc ⁻¹ .

Subscripts.

A,B	catalyst with different porosity distributions.
m	any pore in the catalyst of radius r.
t	any time on-stream (> 50 hours).
o	time initial for pore plugging (= 50 hours).
i	any reactant in the feed.

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Figure 4: Catalyst particle diameter v. effective diffusivity.

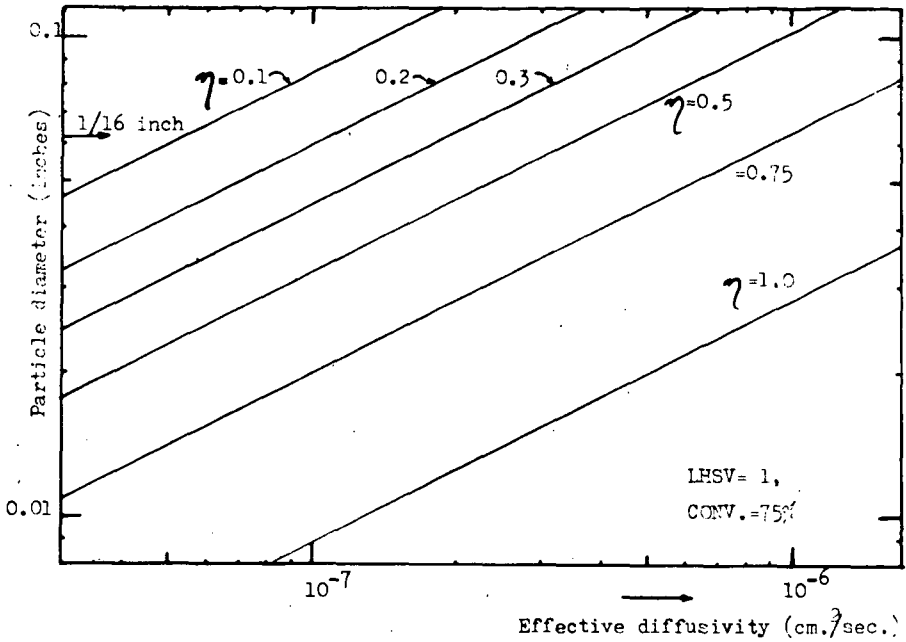


Figure 5: Catalyst pore size distributions.

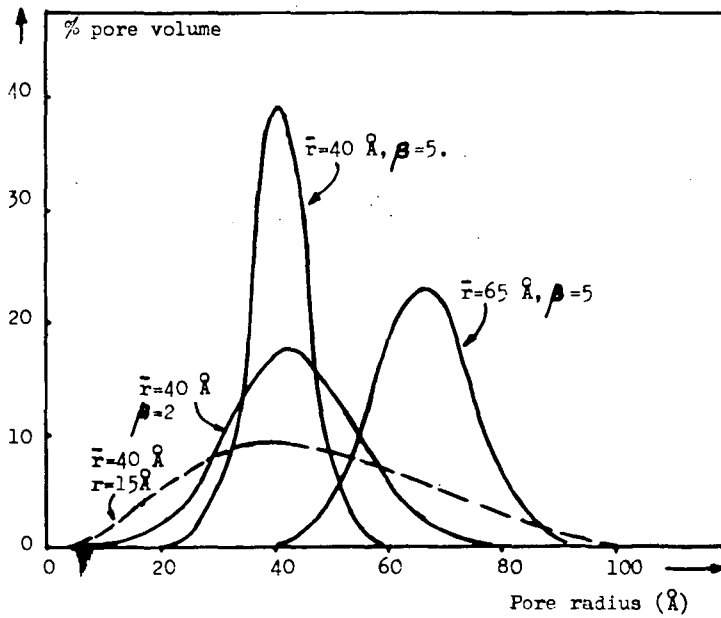


Figure 6: Effect of process conditions on catalyst life

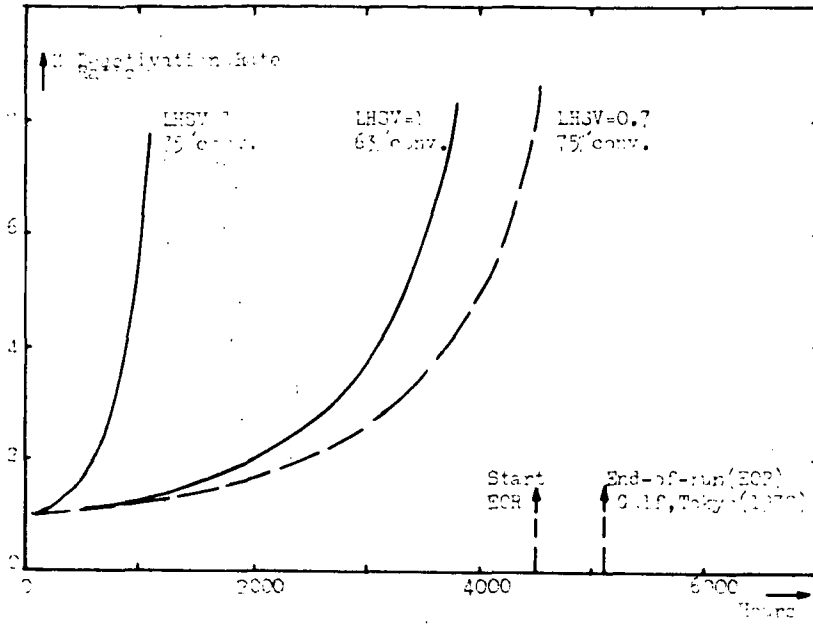
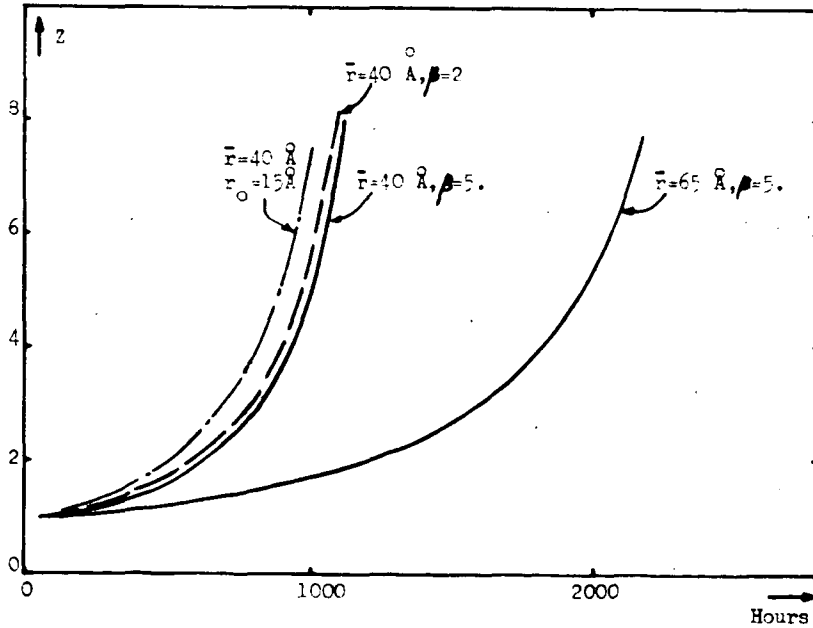
Figure 7: Effect of pore size distributions, \bar{r} -shift.

Figure 8: Effect of macropores, particle size on catalyst life.

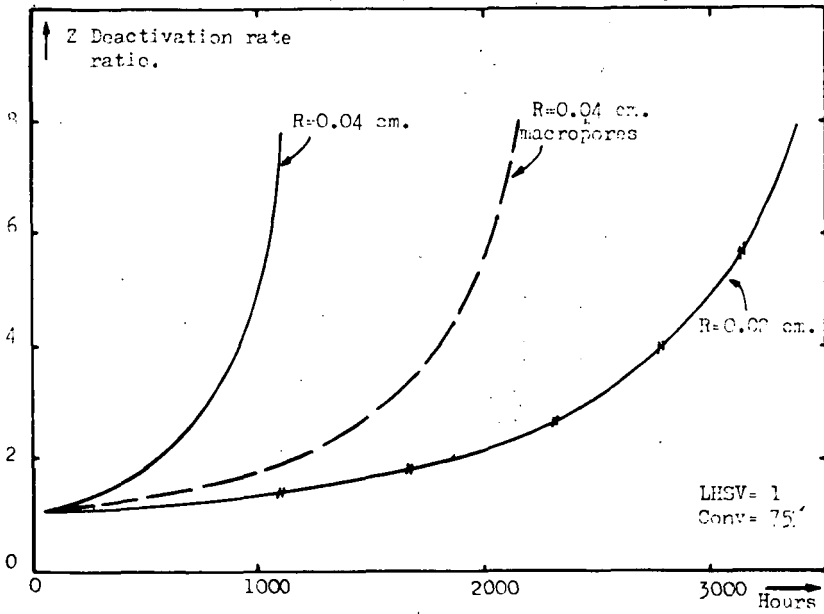


Figure 9: Effects of coke, total pressure on catalyst life.

